

# Dimethyl ether synthesis via methanol and syngas over rare earth metals modified zeolite Y and dual Cu–Mn–Zn catalysts

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## Abstract

A series of zeolite Y modified with La, Ce, Pr, Nd, Sm and Eu were prepared via ion-exchange, and characterized by XRD, FT-IR and NH<sub>3</sub>-TPD. It was found that these rare earth metals were encapsulated in the supercage of zeolite Y and resulted in its enhanced acidity. Among them, La-, Ce-, Pr- and Nd-modified zeolite Y exhibited higher activity and stability (than pure HY) for methanol dehydration to dimethyl ether (DME). For DME synthesis directly from CO hydrogenation using the dual Cu–Mn–Zn/modified-Y catalysts, it was found that Cu–Mn–Zn/La–Y and Cu–Mn–Zn/Ce–Y were more active than Cu–Mn–Zn/pure-HY. The conversion of CO on Cu–Mn–Zn/Ce–HY achieved 77.1% in an isothermal fixed bed reactor at 245 °C, 2.0 MPa, H<sub>2</sub>/CO = 3/2 and 1500 h<sup>−1</sup>.

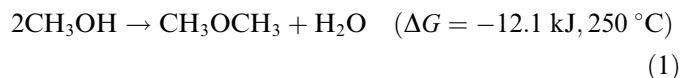
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**Keywords:** Dimethyl ether; Methanol; Zeolite Y

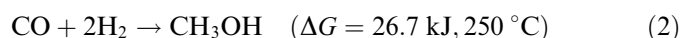
## 1. Introduction

Dimethyl ether (DME) has been utilized as alternate fuel for vehicle engines instead of diesel, and as fuel additive and family cooking gas instead of liquefied petroleum gas (LPG) [1]. Compared with the traditional chlorofluorocarbon (CFCs, Freon) and newer R-134a (HFC-134a), DME and fluoro-dimethyl ether are also widely used in environmental friendly aerosol spray and green refrigerant because of their zero ozone depletion potential (ODP) and lower globe warming potential (GWP) [2]. Therefore, production and utilization of DME have attracted ever-increasing attentions due to both the need of environmental protection and the increased price of crude oil.

DME is traditionally produced via methanol dehydration Eq. (1) catalyzed by liquid sulfate acid (or phosphate acid) and/or solid acids [3–12]:



And methanol is synthesized from CO hydrogenation:

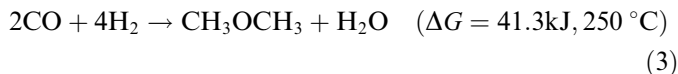


Several solid-acid catalysts such as HZSM-5, H-beta, alumina and SAPOs were reported for methanol dehydration in a temperature range of 250–400 °C [3–12]. However, most of these solid-acid catalysts produce undesirable side products such as hydrocarbons (and coke) due to the presence of strong acid sites and the high dehydration temperature [8,9]. Thus, extensive research has been focused on finding better catalysts that have higher selectivity for the DME formation and less tendency to generate hydrocarbons (and coke formation) [6]. It has recent been found that DME formation is mainly related to these active sites with weak and medium acidity, and those catalysts with strong acid sites may be preferable for coke deposition [6–12]. And the strong acid sites must be diluted (such as modification of ZSM-5 with Na and/or  $\gamma$ -alumina matrix) in order to achieve a high stability against coke formation and formed water [13].

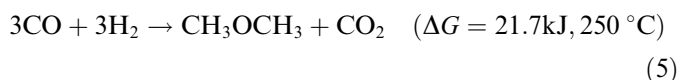
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In addition, recent efforts have focused on the directly synthesis of DME from the synthesis gas ( $\text{CO} + \text{H}_2$ ) using a mechanically mixed methanol synthesis catalyst ( $\text{Cu-Zn-Al}$ ) and methanol dehydration catalyst (alumina or zeolite) in the same reactor, a process termed “synthesis gas to dimethyl ether” (abbreviated as STD) [14–20].



During STD, steam formed in hydrogenation step Eq. (3) reacts quickly with CO via a water–gas shift reaction Eq. (4), and the overall stoichiometric reaction is expressed as follows:



The overall process seems more favorable thermodynamically than the separated methanol synthesis Eq. (2) [21], and very high CO conversion was reported in a temperature-gradient reactor [22]. Moreover, this process also has several advantages in terms of both economical and technical aspects including lower energy requirement.  $\text{CuO-ZnO-Al}_2\text{O}_3/\text{NaHZSM-5}$  bifunctional catalyst exhibits high activity and stability for this process at  $275^\circ\text{C}$  even when  $\text{CO}_2$  is fed and there is a high water concentration in the medium [23,24]. In this process, methanol synthesis and dehydration take place consecutively on the dual catalyst. However, the hydrogenation step (from CO to methanol) and dehydration step (from methanol to DME) must be matched completely in order to achieve a higher DME yield.

Traditionally, the dual catalysts for synthesizing DME from syngas were prepared using a mechanically mixed methanol synthesis catalyst ( $\text{Cu-Zn-Al}$  or  $\text{Cu-Zn-Zr}$ ) and methanol dehydration catalyst ( $\text{Al}_2\text{O}_3$  or zeolite) [14–22]. Up to now, only a few solid acids, such as  $\gamma\text{-Al}_2\text{O}_3$  [15,19–24], HZSM-5 [16–24], silica–alumina [16,18,20], have been utilized as dehydration catalysts for the STD process. Among them,  $\gamma\text{-Al}_2\text{O}_3$  received most attention because of its lower cost and less byproducts. It is also well known that the STD process must be carried out at higher temperature ( $>280^\circ\text{C}$ ) because the acidity of  $\gamma\text{-Al}_2\text{O}_3$  is not strong enough for the consecutive methanol dehydration [15,20–26]. Under such severe conditions, carbon deposition happens on the surface of  $\text{CuO-ZnO-Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  catalyst [23].

However, in theory, this reaction requires a much lower reaction temperature because it is an exothermic process [21]. Consistent with this hypothesis, previous work demonstrated that  $\text{Cu-Mn-Zn/zeolite-Y}$  prepared via a coprecipitation impregnation procedure could catalyze the STD process at  $245^\circ\text{C}$  with a moderate activity, whereas the physically mixed  $\text{Cu-Mn-Zn}$  and  $\gamma\text{-Al}_2\text{O}_3$  must be operated at a higher temperature ( $>260^\circ\text{C}$ ) [25–27].

In this report, the dehydration component (zeolite Y) was modified with several rare earth metals, and used as the catalyst for methanol dehydration and as the dehydration component of the dual catalyst for the DME synthesis. The properties of these catalysts were fully characterized by XRD, FT-IR and  $\text{NH}_3\text{-TPD}$ .

## 2. Experimental

### 2.1. Catalyst preparation

A powder zeolite  $\text{NH}_4\text{Y}$  ( $\text{Si/Al} = 6$ , BET surface area  $420\text{ m}^2/\text{g}$ ) was firstly ion-exchanged in each of an acidic aqueous solution of  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  at  $90^\circ\text{C}$  under reflux for 4 h, then the solid was filtered, washed, dried and finally calcined at  $500^\circ\text{C}$  for 5 h. This process was repeated 3–5 times in order to obtain an equal amount of rare earth metal in the modified zeolite. Atom adsorption spectroscopy (AAS) analysis indicated that rare earth metal in modified zeolite were in 1.9–2.0 wt%. At the same time, each of 2 wt% of  $\text{La}_2\text{O}_3$  and  $\text{CeO}_2$  modified zeolite HY was prepared via mechanically mixing method (denoted as  $\text{La}_2\text{O}_3\text{-HY}$  and  $\text{CeO}_2\text{-HY}$ ), calcined at  $500^\circ\text{C}$  for 5 h and utilized as the reference samples for methanol dehydration and discussion.

Hydrogenation catalyst,  $\text{Cu-Mn-Zn}$  ( $\text{Cu/Mn/Zn} = 2/4/1$  mol ratio), was prepared by traditional coprecipitation method. An aqueous solution containing  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  with the total metal ion concentration of 1.0 mol/L was dropwise mixed with an aqueous solution of  $\text{Na}_2\text{CO}_3$  (0.5 mol/L) under stirring at  $50^\circ\text{C}$ . In the course of coprecipitation, pH was controlled at 10 by the simultaneous dripping of an aqueous  $\text{NaOH}$  solution (3.0 mol/L). This suspension was maintained at  $50^\circ\text{C}$  for 24 h with stirring, then filtered off and washed with distilled water, dried overnight at  $120^\circ\text{C}$  in air and calcined at  $450^\circ\text{C}$  for 3 h.

The dual catalysts were prepared via mechanically mixing of the modified zeolite Y (10 g) and the  $\text{Cu-Mn-Zn}$  catalyst (20 g). A controlled amount of water (about 0.8 g/g-solid) was added in order to make the two components mixed completely. The mixed powder was dried at  $110^\circ\text{C}$  for 5 h, and further calcined at  $450^\circ\text{C}$  for 3 h. These powder catalysts were compressed, ground and sieved to 20–40 mesh for catalytic reaction.

### 2.2. Characterizations

XRD analysis was performed in an automated power X-ray diffraction system ( $\text{Cu K}\alpha$  radiation, 45 kV, 40 mA) (Rigaku RINT 2500, Japan). IR spectra were obtained using the KBr method in a Nicolet 560 (USA) system.

$\text{NH}_3\text{-TPD}$  experiment was performed in an auto-catalytic adsorption system (AMI-200, Zeton Altamira, Pittsburgh, USA), using an on-line thermal conductivity detector (TCD), and quartz tubular reactor. Sample was pretreated at  $500^\circ\text{C}$  in argon flow for 1 h and then cooled

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